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(54) Title: MODIFIED ABSORPTION THROUGH UNIQUE COMPOSITE MATERIALS AND MATERIAL COMBINATIONS

(57) Abstract: In accordance with the present invention, there are provided methods to modulate the energy absorptivity of materials, particularly as the materials are employed in process such as laser-assisted direct materials deposition. Invention methods include combining materials of dissimilar energy absorptivity at a selected wavelength of electromagnetic energy. For example, by combining particles of material that are relatively reflective of electromagnetic energy at a selected wavelength, with materials that are more absorptive at the same wavelength, transfer of energy from the less absorptive material to the material that is more absorptive is facilitated. In this manner, less energy can be used to raise the temperature of the less absorptive material, by taking advantage of energy transfer from the more adsorptive material to that which is less absorptive at the selected wavelength.

# MODIFIED ABSORPTION THROUGH UNIQUE COMPOSITE MATERIALS AND MATERIAL COMBINATIONS

## FIELD OF THE INVENTION

The present invention relates to the fields of metallurgy and direct materials deposition.

## BACKGROUND OF THE INVENTION

Direct Materials Deposition (DMD) processes allow complex components to be efficiently fabricated in small lot sizes to meet the stringent requirements of the rapidly changing manufacturing environment. This process produces three-dimensional parts directly from a computer aided design (CAD) solid model. U.S. Pat. No. 4,323,756 discusses the production of rapidly solidified bulk articles from metallic feedstock using an energy beam as a heat source to fuse the feedstock onto a substrate. Repeated layers are deposited in order to arrive at a three-dimensional finished product. However, the use of a laser to melt material creates excessive heat in the part, causing distortion and residual stress within the part being made. Also, the high energy level of such a laser causes inefficiencies throughout the system.

The use of exothermic and non-exothermic reactions in laser assisted techniques have been disclosed for bonding particles, producing a metal halide, changing optical properties, and changing the state of reflectivity in an optical recording medium. However, none of these prior uses have employed exothermic materials to build a part, or to reduce the laser power required to melt materials, thus reducing problems of residual stress, distortion, and energy inefficiencies. For example, U.S. Pat. No. 5,182,170 discloses a method for selectively sintering a layer of powder to produce a part comprising a plurality of sintered layers. This method uses the reaction between the material in the powder layer (at locations where the powder is irradiated by a laser beam) and reactants in the surrounding atmosphere to form a part. The powder is deposited on a target surface, which is exposed to a reactant gas, and then heated using a laser. The gas atmosphere and the heated powder material cause a reaction to occur. This reaction causes the gas to decompose to a solid and a gas, where the gas adheres to the surface of the powder particles and serves to bond the particles together. All claims of the '170 patent require a powder starting stock that is placed on a target surface. This patent, however, does not use exothermic materials nor does it teach an exothermic reaction.

U.S. Pat. No. 4,332,999 claims the use of a reactive atmosphere in conjunction with the radiant heating of a metallic surface to provide an efficient method of machining. This patent discloses use of a beam of radiant energy upon a workpiece whereby the workpiece is heated at

the area of incidence with the beam. The atmosphere is chemically reactive with the material of the workpiece at the area of incidence. The area of incidence is then heated to a reaction temperature that is below the melting point of the workpiece material. Both conditions are chosen so that the chemical reaction therebetween is exothermic, and the reaction occurs at temperatures above the boiling point of workpiece material. The gas is preferably a halogen or nonmetallic halide, which reacts with the workpiece material to produce a metal halide. In the '999 patent, the exothermic reaction is used to break down metal and remove material, rather than to cause metals to form parts from exothermic reactions.

U.S. Pat. No. 5,459,018 claims the use of alternating layers of metal and oxide, such that the oxide has a standard enthalpy of formation higher than that of the oxide obtained by oxidizing the metal. When the interface region is heated with a laser beam, an exothermic reaction occurs, converting oxide to metal and vice-versa, resulting in changed optical properties. The exothermic reaction in the '018 patent is not used to create a part, but rather to change the state of reflectivity in an optical recording medium.

Exothermic powders have also been used as a source of energy. G. V. Ivanov and F. Tepper in *'Activated' Aluminum as a Stored Energy Source For Propellants* (presented at the Nobel Symposium on Chemical Propulsions, Stockholm, May 28, 1996) and G. V. Ivanov, M.I. Lerner, and F. Tepper in *Intermetallic Alloy Formation from Nanophase Metal Powders Produced by Electro-Exploding Wires* describe the production of exothermic powders by the process of electro-explosion of metal wire (EEW) using aluminum. The result was an activated aluminum referred to as Alex. This activated aluminum contains stored energy that is released when a threshold temperature is reached. Other electro-exploded materials, including copper, silver, and zinc, have been produced. The suggested use of such materials is as a fuel in pyrotechnics, explosives, and propellants. This process has not been applied to any direct material deposition processes.

A need therefor exists in the art for improved materials for use in laser treating processes.

## OBJECTS AND ADVANTAGES

Accordingly, several objects and advantages of the present invention are:

(a) to provide lower laser power requirements in DMD applications;

(b) to reduce distortion of a workpiece caused by use of a high powered laser heat source in the preparation thereof;

(c) to increase energy efficiency throughout DMD systems;

(d) to provide a significant time reduction in producing articles of a unique composition and/or structure;

(e) to enhance the ability to laser deposit high reflectivity materials;

(f) to provide an efficient method to deposit high thermal conductivity materials;

(g) to provide a method to introduce reactive materials such as aluminum for laser deposition without a tenacious oxide material;

(h) to provide bonding between high temperature materials using a low energy source; and

(i) to significantly reduce interstitial voids for powder metallurgy applications.

These and other objects and advantages of the invention will become apparent upon review of the specification and appended claims.

## BRIEF DESCRIPTION OF THE INVENTION

It is often the case that materials desired for use in laser-assisted deposition processes must be subjected to unacceptably high levels of energy in order to render the materials depositable. High energy levels are required because certain materials are largely reflective of electromagnetic energy at the wavelength used to impart the energy required to render the materials depositable. The present invention provides a method to enhance the energy absorption of reflective materials. This is accomplished by combining the reflective material with a material that is more absorptive of electromagnetic energy at the same wavelength than is the reflective material. Without being bound by theory, it is believed that the energy absorbed by the absorptive material is efficiently transmitted to the reflective material by mechanisms such as radiant heat transfer, conduction, or the like.

In another aspect of the invention, there are provided methods to reduce the energy absorptivity of a material that is relatively absorptive of electromagnetic energy at a selected wavelength, by combining the absorptive material with a material that is relatively less absorptive of electromagnetic energy at the same wavelength.

The present invention is amenable to use with any material to which energy must be imparted. In particular, DMD applications are well suited for application of invention methods. The invention methods provide a means to enhance energy absorption into a particular reflective material by combining that material with one or more materials that are more absorptive. These

materials can be a homogeneous mixture of particles of the different materials, a suspension of particles of different materials, particles of one material coated with a second material (i.e., the absorptive material), a combination of the coated particles with another material, and the like. Invention methods allow for reduced energy requirements, which result in substantial energy savings. Due to the lower energy required to render the material depositable, the residual stress of the resulting item is reduced, as is spatial distortion.

Certain combinations of materials provide an additional advantage of forming composites that also possess unique properties. Several advantages of the composites are that the thermal coefficient of expansion can now be tailored to match that of another material and the thermal conductivity of the reflective material can be largely preserved. A further advantage provided through these combinations of materials is to provide a surface that is readily melted by laser such that fully dense structures can be fabricated.

## BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a cross-section of an apparatus for laser-mediated Direct Materials Deposition (DMD).

FIG. 2 is a schematic showing the difference in distortion between a part **10** formed on a deposition substrate **12** from a composite of reflective and absorptive materials, and a part **14** formed on a deposition substrate **12** from conventional processed powders.

FIG. 3 depicts a cross-section of a microstructure comprising a composite material **26**. The dispersed particles **28** are evenly distributed throughout the base material **30**.

## DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there are provided methods to enhance or reduce the energy absorbance of materials at a selected wavelength by combining materials having relative differences in their energy absorbance at the selected wavelength. Thus, in one embodiment of the present invention, there is provided a method to enhance the energy absorption by a material that is reflective of electromagnetic energy at a selected wavelength (i.e., a reflective material), said method comprising combining said reflective material with a material that is more energy absorbent at said selected electromagnetic energy wavelength (i.e., an absorptive material) than said reflective material, thereby obtaining an energy enhanced combination.

In another embodiment of the present invention, there is provided a method to reduce the energy absorption by a material that is relatively absorbent of electromagnetic energy at a selected wavelength (absorptive material), said method comprising combining said absorptive material with a material that is less energy absorbent at said selected electromagnetic energy wavelength (i.e., reflective material) than said absorbent material, thereby obtaining an energy reduced combination.

In all embodiments of the present invention, it is presently preferred that one or both of the types of materials (i.e., reflective or absorptive) are particulate, as further described hereinbelow.

It is contemplated that any combination of two materials can be employed in the practice of the present invention so long as, when compared to one another, one material is relatively reflective of electromagnetic energy at a selected wavelength (i.e., "reflective material") and one material is relatively absorptive of electromagnetic energy at the same wavelength (i.e., "absorptive material"). It is presently preferred that the absorptive material be able to readily impart the absorbed energy to adjacent particles of the reflective material in a manner that is not substantially hampered by the reflectivity of the reflective material. Energy can be transferred from absorptive to reflective materials by, for example, radiant heat transfer, conductive heat transfer, or the like.

In one embodiment of the present invention, particularly when the goal is to enhance the energy absorbance of a reflective material at a selected wavelength of electromagnetic radiation, the reflective material is copper, aluminum, silver, gold, platinum, or the like. Absorptive materials contemplated for use in this aspect of the present invention include carbon (e.g., as graphite, diamond, or the like), tungsten, boron, nickel, silicon, silicon carbide, tin, iron, titanium diboride, and the like, as well as combinations of two or more thereof. when the goal is to enhance the energy absorbance of the reflective material, it is presently preferred that the reflective material be in particulate form when combined with the absorptive material.

In another embodiment of the present invention, particularly when the goal is to reduce the energy absorbance of an absorptive material at a selected wavelength of electromagnetic radiation, the absorptive material is aluminum oxide, silicon carbide, tungsten carbide, titanium carbide, titanium diboride, boron nitride, boron carbide, carbon, chromium carbide, tungsten, molybdenum carbide or the like; and the reflective material is aluminum or copper. Particularly useful combinations of absorptive and reflective materials, respectively, are aluminum

oxide/aluminum; silicon carbide/aluminum; tungsten carbide/aluminum; tungsten carbide/copper; boron nitride/copper; boron carbide/copper; carbon/copper; chromium carbide/copper; tungsten/copper; molybdenum carbide/copper, and the like.

The relative amounts of reflective and absorptive materials can be varied over a very broad range depending on a number of factors, including the desired composition of the end product, the desired properties of the combination, the difference in energy absorptivity between the reflective and absorptive materials, and the like. It is presently contemplated that the combination of reflective and absorptive materials will comprise in the range of about 0.1% up to about 99.9% by volume of the reflective material and in the range of about 0.1% up to about 99.9% by volume of the absorptive material. As will be understood by those of skill in the art, an almost infinite number of sub-ranges within the foregoing ranges may be used in the practice of the present invention, with due consideration being given to the factors mentioned above.

In one aspect of the present invention, when the reflective material is aluminum, combination of reflective and absorptive materials will comprise at least about 1% by volume of the reflective material and in the range of about 0.1% up to about 99% by volume of the absorptive material.

In another aspect of the present invention, when the reflective material is copper, combination of reflective and absorptive materials will comprise in the range of 0.1% up to about 90% by volume of the reflective material and in the range of at least about 10% up to about 99.1% by volume of the absorptive material.

It cannot be overemphasized that a variety of relative amounts of reflective and absorptive materials may be combined in order to achieve the desired results in the application of invention methods. Thus, in another aspect, invention combinations comprise at least about 5% by volume of reflective material. In still another aspect, invention combinations comprise at least about 15% by volume of absorptive material.

In yet another embodiment of the present invention, the reflective and absorptive materials described herein are employed as feedstock materials in a laser-assisted deposition process such as DMD, laser cladding, laser spray, plasma spray, or the like. Three dimensional structures can be manufactured by employing invention combinations in a laser-assisted deposition process. Thus, in one aspect of this embosiment, the laser-assisted deposition process is employed for creation of a three dimensional structure on a substrate. In one aspect, the laser-assisted deposition process is DMD. In this aspect, the DMD process comprises passing the

combination of reflective and absorptive materials through a laser under conditions sufficient to convert substantially all of said first and second materials into a depositable form, and depositing, in a layerwise manner, said combination on said substrate, thereby forming a three-dimensional structure thereon. As those of skill in the art will readily understand, "layerwise manner" means that a layer of the "feedstock materials" (i.e., the reflective and/or absorptive materials as used in a laser-assisted deposition process) is created with each iteration of the process. The layer will vary in thickness according to how much feedstock material is converted into depositable form with each iteration of the process. The thickness of the layer deposited with each pass of the laser can vary from about 10 microns up to about 10 millimeters.

In one embodiment of the present invention, a combination of feedstock materials is employed such that the three dimensional structure under construction is sufficiently absorbing of the energy being imparted at the selected laser wavelength so that the surface layer (i.e., the previously deposited layer) of the article is rendered molten during deposition of the subsequent layer. In this manner, the layer being deposited is more thoroughly bound to the surface of the workpiece than if the materials were being deposited on a "cold" piece.

Because the reflective material absorbs energy imparted initially to the absorptive material, in one embodiment of the present invention, the absorptive material is not molten upon being deposited (i.e., upon impact with the substrate) yet prior to impact with the substrate, it may have had sufficient energy imparted to it to render it molten. In other words, the absorptive material has transferred some of its energy to the reflective material, thereby increasing the energy level of the reflective material while at the same time causing the absorptive material to lose energy, sometimes to the point where the absorptive material resolidifies prior to impact with the substrate.

Feedstock materials (i.e., reflective and/or absorptive materials) contemplated for use in the practice of the present invention include a wide variety of elemental and molecular materials (or precursors thereof) in a number of forms, including, solid, liquid, powder, gel, suspension, solution, aerosol, fine mist, and the like. Accordingly, in one embodiment of the present invention, feedstock material is in a finely divided particulate form. In another embodiment of the present invention, feedstock material is provided in a substantially liquid form.

The feedstock may be supplied with one or more carrier systems. For example, powdered feedstock may be used as a homogeneous mixture of reflective and absorptive particles which is fluidized in a gas stream for delivery to the deposition area. While any

combination of reflective and absorptive materials can be used in the practice of this aspect of the invention, particularly useful combinations for homogenous mixtures include Cu-diamond, Cu-W, Cu-graphite, Cu-Ti-diboride, Ni-Ti-diboride, Ni-Cu, Fe-Ni-Cu, CuSiC, AlSiC, and the like.

In yet another aspect of this embodiment, the homogenous mixture of reflective and absorptive materials may further comprises a vehicle (i.e., a solvent, a diluent, or the like) that is compatible with the intended use of the combination (i.e., DMD, or the like).

In still another embodiment of the present invention, the combination comprises a suspension of the reflective and absorptive materials. Again, a suitable vehicle may be employed that is compatible with the intended use of the combination (i.e., DMD, or the like).

In a presently preferred embodiment, a carrier gas is used to transport particulate materials to the location where they are to be deposited. As such, the particulate materials may be mixed in a single feed unit or transported to the deposition location where they are then mixed during the deposition process. In the deposition region, the particles are passed through a laser beam that causes them to be heated such that they become depositable. It is important that some of the particles and the surface onto which the particles are to be deposited are partially absorbing at the electromagnetic energy wavelength used for the deposition process. This is particularly true if the structure required from the deposit is to be fully dense (i.e., contiguous and substantially void-free). This requirement is not nearly as critical if a porous structure is desired.

Feedstock materials can be provided in the form of powder particles composed of different materials that are mixed to create a homogenous mixture of the powder materials. In addition, the powder can be provided in the form of one material coated with a second material. Additional mixing of the coated particles with uncoated particles can also be used to tailor the particle mixture properties. For creating composite materials, the use of coated particles with conventional processing has been shown to be advantageous to achieve better properties in the composite structure. By combining a highly reflective material with a more absorptive material, such that the combination of materials produces a composite material, the high thermal conductivity typically associated with the highly reflective material can be largely preserved. In addition, altering the combination used to create the composite will alter the thermal coefficient of expansion of the deposited structure. This can be particularly advantageous when including the composite structure within yet another material structure. An example of this would be in a

tooling application when a high thermal conductivity material is initially deposited and then is covered by a surface layer of tool steel. As such a tool is thermally cycled it is important that the tool steel and the highly thermally conductive material expand and contract at approximately the same rate to avoid delamination.

When powdered (i.e., particulate or finely divided) materials are used in the practice of the present invention, the size of the particles of which the powder is composed may vary infinitely, dictated only by the level of detail required in the deposited material and the energy required to melt the particle or otherwise impart sufficient energy to the particle to render it depositable on the chosen substrate. The smaller the particle, the less energy required to render it depositable. In addition, greater resolution is achievable with finer particles. Accordingly, powder feedstock material contemplated for use in the practice of the present invention comprises particles in the range of about 5 μm up to about 400 μm. In a presently preferred embodiment, feedstock particle sizes are in the range of about 20 μm up to about 150 μm.

As will be understood by those of skill in the art, the term "depositable form" refers to form whereby the material is suitable for deposition upon and adherence to a substrate or underlying layer of deposited feedstock. The depositable form of a feedstock material may vary according to the feedstock material used, the number of feedstocks applied, the substrate material, and the like. Accordingly, in one embodiment of the present invention, the depositable form of feedstock material will be a heated feedstock. The heating will occur due to energy being imparted by the laser beam(s) through which the feedstock passes immediately prior to and during its deposition on the substrate. In a preferred embodiment, the feedstock will have sufficient energy imparted thereto so that it is softened (e.g., when feedstocks such as glass, and the like are employed). In an even more preferred embodiment, the feedstock will have sufficient energy imparted thereto so that it is heated above the latent heat of fusion for the particular feedstock material employed. In an especially preferred embodiment, the feedstock will have sufficient energy imparted thereto by the laser beam(s) so that it is rendered molten prior to impact with the substrate. Thus, a depositable feedstock may have any one of a number of forms, depending on the composition of the feedstock. Such forms include liquid, gel, slurry, mush, and the like as well as combinations thereof. For example, the absorptive material may take on one form and the reflective material another, yet the combination will be depositable.

Feedstock material may also be provided in the form of feedstock precursors. Accordingly, in another embodiment of the present invention, the electromagnetic energy heats

one or more feedstock material precursors resulting in a chemical conversion of the feedstock material precursor to a depositable form.

Electromagnetic energy may be from a number of sources. Because the present invention is particularly well suited for laser-assisted deposition processes, in one embodiment, the source of electromagnetic energy is a laser. It is further contemplated that the combination of reflective and absorptive materials will be contacted with a laser under conditions sufficient to convert substantially all of the reflective material into depositable form. In certain aspects of the invention, it may be desirable to also convert a portion of the absorptive material into depositable form. In a further embodiment of the present invention, reflective and absorptive materials are alloyed or rendered into a composite material as a result of the contact with the laser, and are both thereby converted into a depositable form. Alloys to be formed include any one or more of Cu-Sn, Al-Sn, Ag-Sn, Au-Sn, Pt-Sn, or the like.

Those of skill in the art can readily determine how much energy is imparted to absorptive particles of material. For example, calculations can be performed by making the following assumptions (which do not necessarily apply to all embodiments of the present invention): (1) the laser irradiance is constant over the diameter of the beam; (2) the particle area of absorption is represented by the cross-sectional area of the particle; (3) the absorption is constant across this area and is independent of the angle of incidence; (4) the particle passes through the center of the laser beam; (5) the beam diameter does not change in the region of the beam the particle passes through; and (6) the absorption of the particle does not change with time or temperature. The time of flight ($t_f$) of the particle through the laser beam can be determined from equation (I) as follows:

$$t_f = \frac{2w_0}{v_p \sin \theta}$$

**(I)**

where $w_0$ is the laser beam radius at the focal point of the beam, $v_p$ is the feedstock particle velocity and $\theta$ is the angle of trajectory of the feedstock particle with respect to the laser beam axis. The energy imparted by the laser beam to the particle is derived by taking the ratio of the area of the particle to the area of the laser beam and then multiplying this quantity by the laser power and the time of flight of the particle through the beam, as given by equation (II) as follows:

$$E_p = \frac{P_l r_p t_f \alpha}{w_0^2}$$

(II)

where $P_l$ is the laser power in watts, $r_p$ is the radius of the particle in mm and $\alpha$ is the absorption of the particle. Equation I indicates that the energy absorbed by a feedstock particle is directly proportional to the time of flight ($t_f$) of the particle through the laser beam. Accordingly, by adjusting parameters to maximize the in-laser $t_f$ of feedstock particles, the energy imparted to the feedstock particles is enhanced. Equation I also demonstrates that in-laser $t_f$ can be increased by a number of means including one or more of reducing particle velocity ($v_p$), decreasing the angle of incidence ($\theta$) of the particle to the laser, increasing the radius of the laser beam at the focal point, and the like.

As will be further understood by those of skill in the art, energy will be imparted to the substrate from the energy contained in the laser-treated feedstock material. As a result, care should be taken to avoid overheating of the substrate which could cause interfacial damage (i.e., surface modification) due to residual stresses caused by any number of factors, including differential thermal coefficients of expansion between the substrate and feedstock, different melting temperatures of feedstock materials, and the like. Accordingly, in a presently preferred embodiment of the present invention, sufficient energy is imparted to the feedstock materials in-flight to render the feedstock depositable and promote adhesion to the substrate without causing significant interfacial damage of the substrate or deposited feedstock. Thus, a function of invention methods is to provide a means to efficiently render depositable the materials (i.e., feedstock) being applied to a substrate while only providing sufficient peripheral heating of the substrate to facilitate adhesion without a significant level of surface modification. In this approach several advantages will be realized. For example, residual stress will be minimized, and thus, a broader range of materials can be deposited onto dissimilar materials.

Substrates suitable for use in the practice of the present invention are well known to those of skill in the art.

Another added benefit of the present invention is a result of the fact that the more energy absorptive material is rendered molten more quickly than the reflective material at a given wavelength of electromagnetic energy. As a result, upon exposure of the absorptive material to sufficient energy to render it molten, the absorptive material can coat particles of the as yet solid

reflective material, thereby enhancing the wettability between the particles of the reflective material. Accordingly, in another embodiment of the present invention there is provided a method to enhance the wettability, at a selected wavelength of electromagnetic energy, of a reflective particulate material that is reflective of electromagnetic energy at said selected wavelength, said method comprising combining said reflective particulate material with an absorptive material that is more energy absorbent at said selected electromagnetic energy wavelength than said reflective material, thereby obtaining a combination wherein said reflective material has enhanced the wettability at said selected wavelength of electromagnetic energy when compared to particles of said reflective particulate material that have not been combined with said absorptive material.

In one aspect of the foregoing embodiment, the reflective material is Al, and the relatively less reflective (i.e., more absorptive) material is one or more of nickel, iron, copper or titanium. In another aspect, the reflective material is Cu and the more absorptive material is one or more of nickel, iron or titanium.

Because the materials combinations of the present invention are useful when they are to be exposed to electromagnetic radiation of a wavelength typically used in DMD applications, in another embodiment of the present invention, there is provided in a DMD process, the improvement comprising combining a particulate feedstock material that is reflective of electromagnetic energy at a selected wavelength with one or more feedstock material(s) that is more energy absorbent at said selected electromagnetic energy wavelength than said reflective material. Combinations of reflective and absorptive materials described herein are all useful in the practice of this embodiment of the present invention.

Laser processing of highly reflective materials often presents a difficult problem. Although higher power lasers can be used to overcome the reflection associated with these materials, this brute force approach presents other problems. From an economic standpoint, the cost associated with a higher power laser can be significant. As an example, if one considers that the reflectivity associated with copper at the Nd:YAG wavelength is 98%, then the total absorbed energy is only 2%. This process is very inefficient when using these conditions. If however the absorption of the copper could be increased without compromising the desirable properties of a copper material, a more efficient process could be developed. This is a problem associated with direct material deposition processes where powdered materials are used.

There are several approaches that could be used to increase the absorption of highly reflective materials during laser processing. One simple method to increase the absorption of the normally highly reflective material is to simply apply a coating that enhances absorption of the powdered materials at the laser wavelength. This method works well to increase the absorption of the powder particles; however, if the coating is vaporized during the heating process then the changing reflectivity is short-lived. This method works well to apply melted powders to a surface, however, a sufficient volume of absorptive material must be used to insure that the deposited surface is also absorptive. Otherwise, the surface quickly becomes reflective and resistant to further laser processing. If the materials used to form the coated particles form a composite material in the deposited structure, then the properties of the deposited material may be altered to provide several advantages. In the composite material, the thermal conductivity of a highly thermally conductive material can be largely preserved and tailored by changing the composition. The thermal coefficient of expansion can be altered as a function of composition. As an example, a copper-tungsten composite can be deposited onto a tool steel surface to provide a means of removing heat from the tool quickly. The expansion of the composite can be closely matched to that of the tool steel and the thermal conductivity of the copper-tungsten composite can be close to that of the copper by itself. This is quite different than if an actual alloy is formed.

A second method that can be used to enhance the absorption of highly reflective materials would be to mix these materials with other materials that are more absorbing at the laser wavelength. If the material which is much more absorbing at the laser wavelength, is dissolved, thus forming an alloy with the more highly reflective material, then the desirable properties of the highly reflective material may be altered. A positive aspect to this approach, however, is that the alloy material deposited onto the substrate will remain absorbing at the laser wavelength.

To maintain the original material properties of the highly reflective materials while still enhancing the absorption of the reflective materials at the selected laser wavelength, a third alternative is available. Through alloying, desirable material properties such as thermal conductivity can be degraded significantly. If however, a coating or absorptive material, whose absorption is significant at the laser wavelength, is selected such that the material with the higher absorption does not vaporize or go into solution, but instead precipitates upon solidification to form a composite of two single phase materials; then when the absorptive material is laser processed together with the more highly reflective material, a unique mixture of materials can be obtained. If the material that possesses the higher absorption at the selected laser wavelength has

carefully been selected, this combination of materials can be used to create a composite material. Materials may be selected based on such criteria as melting temperature, vaporization temperature, solubility between the materials, and the like.

Although the material properties of the highly reflective material can be degraded when it is used to form a composite material, there are many material combinations available to form composites that preserve the desirable properties of the reflective material. Several combinations of material systems that provide this advantage include: copper-tungsten, copper-graphite, copper-silicon carbide, aluminum-silicon carbide, and the like. Some combinations of materials can actually enhance the properties of the highly reflective material when used as composites while at the same time providing an increase in the absorbed laser energy. One such combination of these materials includes copper combined with synthetic diamond particles. In this case, the composite material actually has a higher thermal conductivity than the copper by itself. This particular metal matrix composite can, in fact, have a thermal conductivity that is 50% greater than that of silver. In FIG. 3 a schematic representation for a composite structure is shown. For this set up, the base material **30** (e.g., copper) forms the material that binds the structure together. The particles of the second material **28** (e.g., diamond) form fine particles and help to strengthen the structure **26**.

One of the noteworthy aspects of this invention is the use of various material combinations to produce composite structures that can be fabricated using laser processing. Although this is not an absolute requirement, it is presently preferred that the combination of materials used to form a composite be selected so as to conserve the desirable properties of the material that may not otherwise be readily processed by lasers (i.e., the more reflective material).

In addition to providing an advantage in laser processing of reflective materials, other advantages may also be obtained using the composite structures. For example, if a tool steel is to be deposited onto a copper material with the copper used to form cooling passages, the difference in thermal expansion between these two materials can present a significant problem as the tool is thermally cycled. If such a tool is used for injection molding of plastic components, then the tool can actually be cycled several million times. In this situation, the differences and thermal expansion between the tool steel and the copper can actually cause the mold surface of the tool to pull away from the copper. In addition to preserving the high thermal conductivity of the copper material, a composite structure also allows the thermal coefficient of expansion to be altered to match that of the tool steel. This is an added advantage that the composite structures provide. The difference in thermal expansion becomes even more critical for higher temperature

applications such as die casting, or the like. Reference is made to Figure 2 which demonstrates the type of warping that can occur when materials with dissimilar coefficients of thermal expansion (i.e., materials **14** and **12**) are bonded, versus bonding invention composites **10** with a substrate **12'** having a similar coefficient of thermal expansion.

Experiments have been performed to demonstrate the advantages of the present invention. Structures have been fabricated using copper combined with both metallic tungsten and graphite powders. Whereas previous work has shown that copper by itself is very difficult to process, a copper composite was much more easily deposited. The laser power required to deposit the copper composite was decreased by at least half the amount required for copper by itself. In addition, the deposition rate was increased at the same time.

The invention will now be described in greater detail by reference to the following, non-limiting examples.

## EXAMPLES

Example 1

*Demonstration of the superior properties of aluminum coated with nickel.*

Historically, aluminum has proven to be quite challenging for use with a DMD process. The deposited structures formed globules during the deposition process and the surface oxide associated with these globules inhibited wetting between the different globules.

Nickel coated aluminum particles were placed in a powder feed unit and delivered to the deposition surface in a carrier gas stream. The deposition process was carried out inside of a controlled atmosphere box. When the nickel coated aluminum particles were heated with the laser they immediately formed a uniform layer much more characteristic of other metals that are not limited by their surface oxide layers. These aluminum particles were easily processed using the laser deposition process.

Example 2

*Demonstration of the creation of porous structures using copper coated with nickel.*

In order to demonstrate the superiority of particles of nickel-coated copper particles in a laser-assisted deposition process, the particles were exposed to a Nd:YAG laser and deposited onto a stainless steel substrate to form a ½ inch cube. The nickel coated particles were readily

melted as they passed through the laser beam. Upon impact of the nickel-copper material with the substrate, a three dimensional structure was formed. Once these particles formed a couple of layers on the surface of the stainless steel substrate, the surface became highly reflective and the resulting structure was very porous. Thus, less energy can be used to melt nickel-coated copper particles than uncoated copper particles, yet the properties of the finished item are more like copper, than nickel.

The results of this experiment demonstrate that the more absorbing nickel coating provides a means to melt the copper particles and yet left the surface sufficiently reflective due to the copper particles. Since the surface was reflective, there was insufficient energy absorbed into the substrate to produce a fully dense structure. These results suggest that a combination of particle heating and substrate heating is required to achieve the best processing results. The use of coated particles provides a means to produce a porous structure. In addition, by using a more reflective coating on a material that is normally highly absorbing, a balance may be obtained to inhibit overheating of the highly absorbing materials.

Example 3

*Demonstration of the creation of dense structures using a combination of nickel-coated copper and tungsten.*

In order to demonstrate the superior performance properties of a combination of nickel-coated copper and tungsten, nickel coated copper particles were mixed with a tungsten powder and the combination then formed a usable material for direct deposition. Tungsten was added to the mixture in an amount of from about 12-15% by volume, although lower volume percentages of tungsten may be employed. Tungsten is approximately 40% absorbing at the selected Nd:YAG laser wavelength (1.064 μm), and thus provides a sufficient change in the absorption of the deposited layer to allow a fully dense structure to be achieved. In addition, metallographic cross-sections show that there are tungsten precipitates within the solid structure, thereby demonstrating the ability to achieve composite materials using invention methods.

Example 4

*Demonstration of the superior properties of copper-coated tungsten*

Copper coated tungsten particles (approximately 25 volume percent tungsten) were tested to determine if particles of relatively absorptive tungsten could be coated with more reflective

material and still allow structures of sufficient structural integrity to be fabricated. Deposits formed using this material show a more uniform distribution of tungsten particles within the copper matrix than if mixed but uncoated materials are used. Metallographic cross-sections show that this structure is also fully dense.

While the invention has been described in detail with reference to certain preferred embodiments thereof, it will be understood that modifications and variations are within the spirit and scope of that which is described and claimed.

**WHAT IS CLAIMED IS:**

1. A method to enhance energy absorption by a particulate material that is reflective of electromagnetic energy at a selected wavelength, said method comprising combining said reflective material with a material that is more energy absorbent at said selected electromagnetic energy wavelength than said reflective material, thereby obtaining a combination.

2. The method according to claim 1, wherein:
   a) said electromagnetic energy is supplied by laser,
   b) said material is used in a laser-assisted deposition process, and
   c) said combination is contacted with said laser under conditions sufficient to convert substantially all of said reflective material into depositable form.

3. The method according to claim 2, wherein reflective and absorptive materials form an homogeneous mixture, whereby upon deposition or upon deposition and subsequent heat treatment, a composite material is formed.

4. The method according to claim 3, wherein said combination is Cu-diamond, Cu-W, Cu-graphite, CU-Ti-diboride, Ni-Ti-diboride, Ni-Cu, Fe-Ni-Cu, CuSiC, or AlSiC.

5. The method according to claim 2, wherein said laser-assisted deposition process is direct materials deposition process (DMD), laser cladding, laser spray, or plasma spray.

6. The method according to claim 5, wherein said DMD process is employed for creation of a three dimensional structure on a substrate.

7. The method according to claim 6, wherein said DMD process comprises:
   a) passing said combination through a laser under conditions sufficient to convert substantially all of said reflective and absorptive materials into a depositable form, and
   b) depositing, in a layerwise manner, said combination in a depositable form on said substrate, thereby forming a three-dimensional structure thereon.

8. The method according to claim 7, wherein the three-dimensional structure is sufficiently absorbing of energy at said laser wavelength such that a surface layer of said deposited combination is melted during deposition of the next layer of materials.

9. The method according to claim 7, wherein said absorptive material is not molten upon being deposited on said substrate yet wherein said absorptive material has, in step (b), absorbed energy sufficient to melt.

10. In a DMD process, the improvement comprising combining a particulate feedstock material that is reflective of electromagnetic energy at a selected wavelength with one or more feedstock material(s) that is more energy absorbent at said selected electromagnetic energy wavelength than said reflective material.

11. The method according to claim 10, wherein said particulate feedstock material that is reflective is Al or Cu.

12. The method according to claim 11, wherein, when said particulate feedstock material that is reflective Cu, said feedstock material that is absorptive is nickel, copper, titanium, titanium diboride, diamond graphite, silicon carbide or iron.

13. The method according to claim 11, wherein, when said particulate feedstock material that is reflective Al, said feedstock material that is absorptive is silicon carbide.

14. A method to enhance the wettability at a selected wavelength of electromagnetic energy of a reflective particulate material that is reflective of electromagnetic energy at said selected wavelength, said method comprising combining said reflective particulate material with a material that is more energy absorbent at said selected electromagnetic energy wavelength than said reflective material, thereby obtaining a combination wherein said reflective material has enhanced the wettability at said selected wavelength of electromagnetic energy when compared to particles of said reflective particulate material that have not been combined with said absorptive material.

15. The method according to claim 14, wherein said reflective particulate material is Al and wherein said absorptive material is nickel, iron, copper or titanium.

16. The method according to claim 14, wherein said reflective particulate material is Cu and wherein said absorptive material is nickel, iron or titanium.

17. The method according to claim 1, wherein said combination comprises an homogenous mixture of said reflective and absorptive materials.

18. The method according to claim 17, wherein said homogenous mixture comprises a solution containing said reflective and absorptive materials.

19. The method according to claim 18, wherein said solution further comprises a vehicle.

20. The method according to claim 17, wherein said reflective material is particulate and wherein particles of said reflective material are coated with said absorptive material.

21. The method according to claim 1, wherein said combination comprises a suspension.

22. The method according to claim 1, wherein said reflective material is copper, aluminum, silver, gold or platinum.

23. The method according to claim 1, wherein said reflective material is copper and said absorptive material is diamond, graphite, tungsten or silicon carbide.

24. The method according to claim 1, wherein said combination comprises at least about 5% by volume of said reflective material.

25. The method according to claim 24, wherein said reflective material is copper.

26. The method according to claim 1, wherein said combination comprises at least about 15% by volume of said absorptive material.

27. The method according to claim 1, wherein said combination absorbs energy at the selected wavelength more efficiently than said reflective particulate material alone.

28. The method according to claim 1, wherein said absorptive material forms an alloy or composite with said reflective particulate material.

29. The method according to claim 28, wherein said alloy is Cu-Sn, Al-Sn, Ag-Sn, Au-Sn or Pt-Sn.

30. A method to reduce the energy absorption by an absorptive material that is absorptive of electromagnetic energy at a selected wavelength, said method comprising combining said absorptive material with a reflective material that is less energy absorbent at said selected electromagnetic energy wavelength than said first material, thereby obtaining a combination.

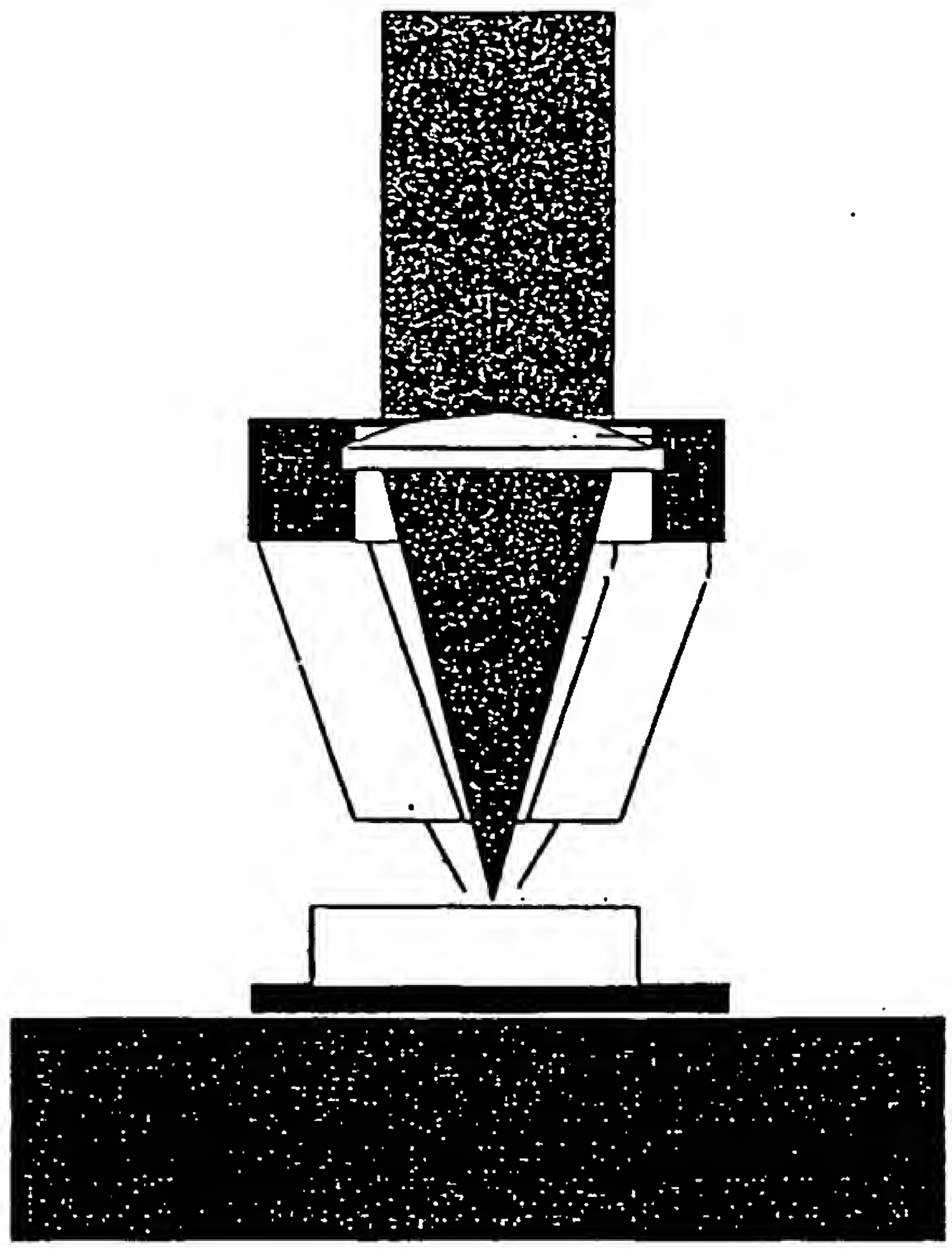

Figure 1

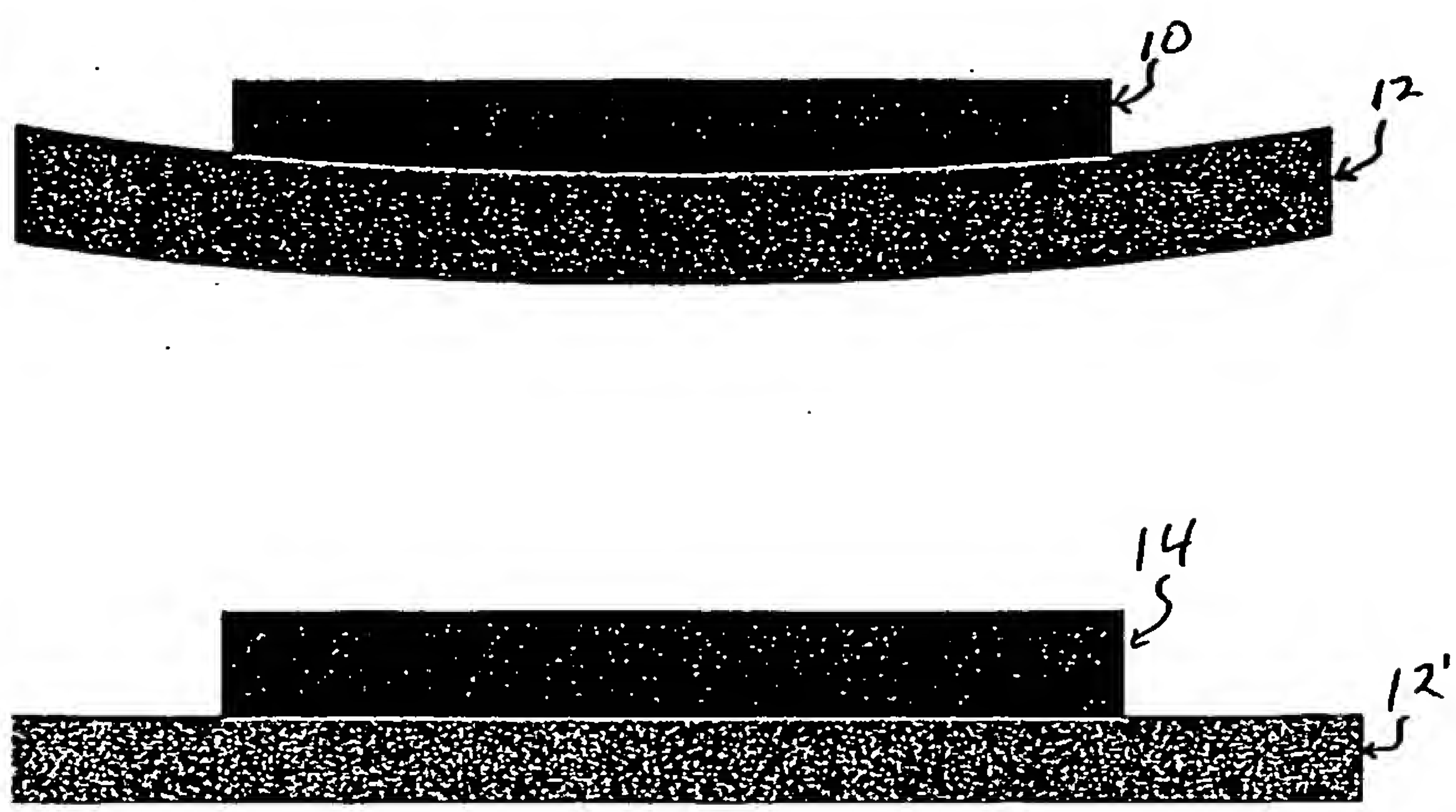


Figure 2

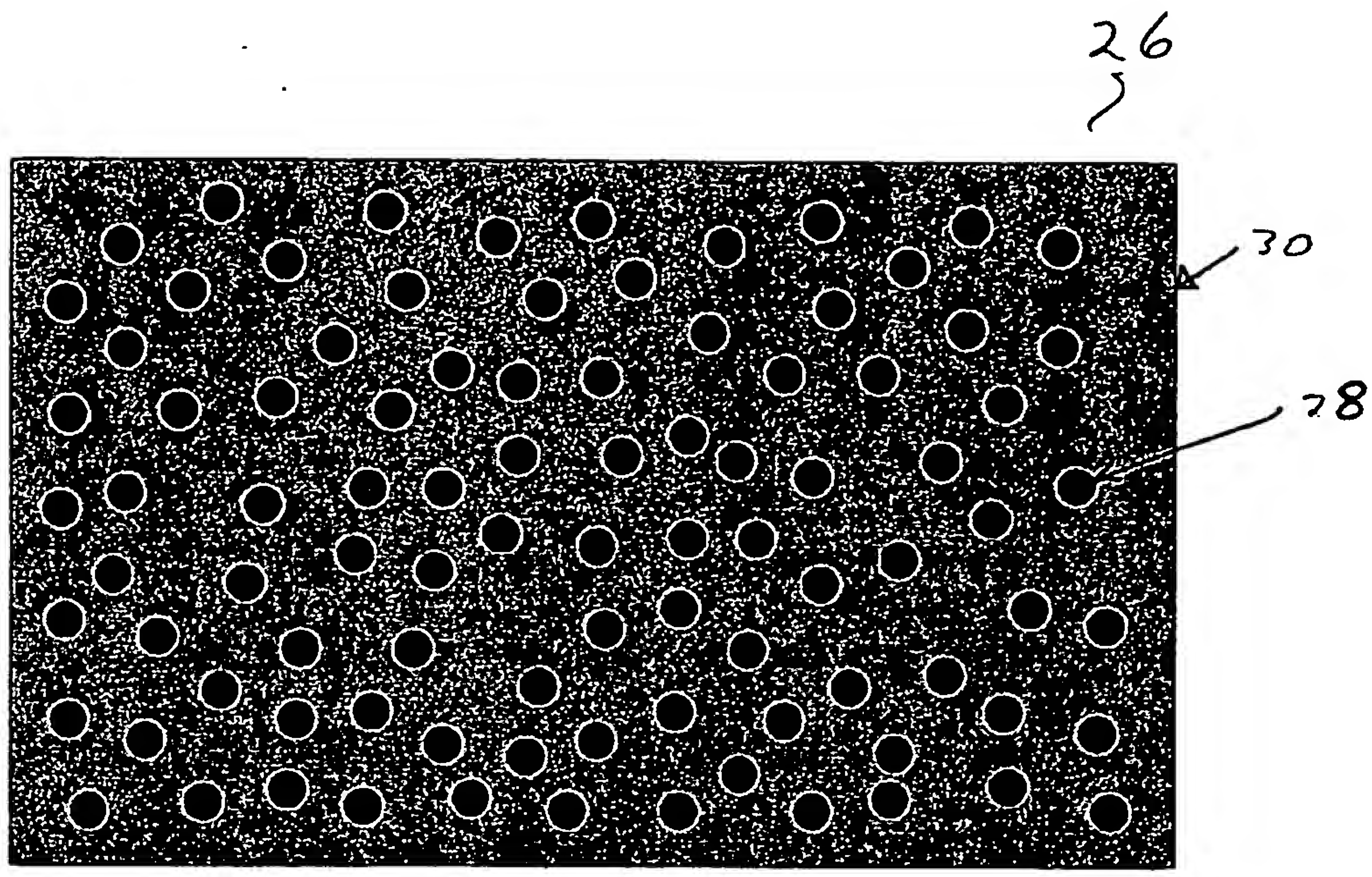


Figure 3